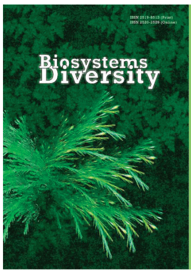

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Nanotechnologies in crop cultivation: Ecotoxicological aspects

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The European Commission has recognized nanotechnologies as extremely promising for increasing competitiveness of different sectors of the economy. On account of climate changes and the quest for food security, they are an effective way of solving key problems in the agrarian sector. Nowadays nanotechnologies are widely used for creating nanofertilizers, nanoinsecticides, nanofungicides, nanoherbicides and other nanopreparations. Numerous researches affirm advantages of nanopreparations, which has helped them find a wide use in agricultural practice. At the same time, nanopreparations are the source of entry into the environment of nanoparticles (size less than 100 nm) which are characterized by large active surface and specific physical-chemical properties different from ordinary chemical substances. It is precisely this which determines their bioaccessibility, bioaccumulation and toxicity. Recently, data about toxicity of nanoparticles for human and natural ecosystems have been accumulated. The results of a great deal of research affirm that they break the processes of photosynthesis, transpiration, mitosis, miosis and have a negative influence on colouring agents, proteins and carbohydrates. Under their action, physiological processes of plant growth and development are disturbed, which take place mainly in root system. Nanoparticles are characterized by high bioaccessibility for soil organisms, they are toxic to earthworms and microorganisms and they influence circulation of carbon and nitrogen. Aquatic organisms have been shown to have high sensitivity to nanoparticles; toxic effect has been registered for fish, daphnids, water plants and microorganisms. Taking into consideration the high level of potential danger of nanopreparations used in crop cultivation, special notice should be paid to the development of eco toxicological research. At present, nanoecotoxicological approaches to assessment of the danger of nanomaterials and nanoparticles are absent. Development of reports on elaboration of quantitative and qualitative methods of analysis, and methods of modeling and prognostication of risks is only at the initial stage. The objective of this review is attracting attention to solving the problem of nanoecotoxicology, nanoagrochemicals and nanopesticides, which needs consolidated efforts of scientists, governmental organizations and business and is an obligatory condition for preventing the negative impact of nanomaterials on humans and the environment.

Keywords: nanotechnology; nanomaterials; nanoparticles; environmental; nanoecotoxicity; agriculture.

Introduction

Nanotechnologies are recognized by the European Commission as one of six "key favourable technologies", which increase competitiveness of different sectors of the economy (OECD Test Guidelines for the Chemicals, 2018). Analysis of scientific literature allows one to say confidently that nanotechnologies have found their use in all fields of human activity such as physics, chemistry, medicine, agriculture, pharmacology, cosmetics industry, biosensors etc. Nowadays more than 400 companies are active in the field of nanotechnologies and their number is expected to increase to 1,000 and more in the next 10 years (Som et al., 2011). Assessment of the production market of nanomaterials (ENMs) shows that in 2020 it will be 1,663168 tons comparative to 270,041 tons in 2012 (He et al., 2015).

One of the spheres of human activity where nanotechnologies has taken an important place is agriculture. On account of climate changes and the quest for food security, nanotechnologies are an effective way of solving key problems in the agrarian sector (OECD Test Guidelines for the Chemicals, 2018). In particular they are widely used in increasing crop productivity, protecting plants from pests, diseases and weeds (Nair et al., 2010; Pete et al., 2010; Singh Duhan et al., 2017).

In spite of the evident advantages of nanotechnologies, there is a pending issue about influence of nanomaterials and nanoparticles (NPs), which are parts of them, on human health and the environment. Works by many authors show their negative influence on the human organism. In particular, through the act of breathing nanoparticles easily enter the lymphatic, blood circulatory and nervous systems, brain and other tissues and organs and disturb their normal functioning (Viswanath & Kim, 2017). Nanomaterials enter the environment and interact with biotic and abiotic components. They can have negative influence on higher plants and organisms living in the natural environment (Aruoja et al., 2015; Böhme et al., 2015; Singh Duhan et al., 2017).

Appearance of nanoparticles in the soil, water and air can harm both human ecological biota and. At present all risks connected with nanomaterials are unknown, which disquiets scientists, the public and authority. There is a vast gulf between the knowledge of physical-chemical properties of nanomaterials and knowledge about their influence on environment and human health. It is supposed that under interaction with environmental components, such as chemical substances, bacteria, biological pollutants etc., behaviour of nanomaterials changes significantly, which can lead to unpredictable results. Thus characteristics of certain environments have to be taken into account in determining nanotoxicological risks (He et al., 2015).

Scientists accentuate that discovering risks from nanomaterials and nanoparticles is a crucial question (Viswanath & Kim, 2017). Toxicity of nanomaterials must be examined and the performing of these experiments must be the basis of their safety for humans and the environment. On account of possibility of long-term influence of low concentrations of nanomaterials, serious attention must be paid to the remote effects and adaptation of organisms to nanotoxicity. Nanoparticles which are parts of nanomaterials differ from common pollutants so the methodology of nanoecotoxicology has to be specific. Development of such methodology must be the main task for representatives of science, government and business on the current stage of the development of nanotechnologies (Hu et al., 2016; Costa & Fadeel, 2016).

Positive aspects of using nanotechnologies in agriculture

Nanotechnologies are technologies due to which material on atomic level (from 1 to 100 nanometres) are developed. With nanotechnologies scientists use atoms and molecules for developing new materials, components or systems with improved or new properties. In agricultural practice, nanotechnologies are successfully used for developing a large number of nanomaterials for agricultural crops. They are fertilizers, plant growth regulators, pesticides (insecticides, fungicides and herbicides) and others. Preparations obtained under use of nanotechnologies contain nanoparticles, which are less than 100 nm, and characterized by large active surface and unique physical and chemical properties (Jefferson, 2000; Auffan et al., 2009; Ghormade et al., 2011).

For creating nanoagrochemicals, nanopesticides and nano plant growth regulators, nanoparticles of Ce, Zn, Mo, Ag, Au, Al, Fe (Raliya & Tarafdar, 2013; Siddiqui & Al-Whaibi 2014; Jasim et al., 2016), polymers, magnetic materials, quantum dots and others are used (Singh Duhan et al., 2017).

Nanoagrochemicals. Nanofertilizers are created to implement different functions for ensuring plants with nutrients, regulating the processes of prolonging the provision of nutrients from fertilizing to the soil.

Nanosurface of fertilizers ensures their protection from quick solution in soil. It favours slow freeing of nutrients from fertilizer granules and delivering them to plants (Santoso et al., 1995). Using slow freeing of nutrients from nanofertilizers became the way of minimizing environmental pollution, which is especially important in conditions of global environment pollution (Wu et al., 2005; Wu & Liu, 2008).

Surface electric charge of active nanoparticles ensures their better adhesion to the surface of plant organs and quick penetration into plant cells. Treatment of plants with nanopreparations activates primary plant development and helps overcome consequences of climatic and pesticide stress at the beginning stages of development (Branton et al., 2008). It has been determined that in many cases nanoparticles favour plant root system growth and increases the area of nutrition (Tripathi & Sarkar, 2014). Carbon nanodots (wsCND) had positive influence on wheat growth (root), were not toxic for plants of wheat, led to increasing crop productivity. Multilayer wsCND in concentration of 50–200 μg/mL under treatment of the seeds had positive influence on germination of barley, soybean and corn. The root system grew by 26%, leaf surface by 40% comparing to control. The authors of this research recommend using carbon nanotubes as plant growth regulators (Lahiani et al., 2013).

Nanotechnologies have a great value for effective use of biofertilizers. Biofertilizers contain microorganisms, which are very sensitive to environmental conditions such as temperature and humidity. A polymeric nanoparticle for covering biofertilizers favours their tolerance to unfavourable environments and longer maintainance (Wu et al., 2005; Jha & Prasad, 2006). Nanoparticles of gold increase crop productivity, they don't have a negative influence on soil organisms (Shukla et al., 2015).

Nanotechnologies are used for providing plants microelements – Zn, Fe, Mo, Cu and others. They are introduced to the soil, where they penetrate the plant roots and then penetrate the leaf surface (Peteu et al., 2010). Using nanopreparations allows the problem of microelements deficiency in the soil to be solved. In limestone soils under high value of pH, deficiency of Fe for wheat was overcome by spraying crops with nanoparticles of FeO (Bakhtiari et al., 2015). Positive results from using nanoparticles of FeO were recorded on agricultural crops (soybean and pea) (Ghafariyan et al., 2013; Delfani et al., 2014). Using nanopreparations of manganese increased photosynthesis activity of legumes (Pradhan et al., 2013).

Using NPs-Al stimulated root growth of *Raphanus sativus* and *Brassica napus* (Lin & Xing, 2007), NPs-Au have a positive influence on germination index of *Cucumis sativus* and *Lactuca sativa* (Barrena et al., 2009), NPs-CeO_2 improved the conditions of root and stem growth, favoured biomass accumulation of *Zea mays* and *Coriandrum sativum* (Lopez-Moreno et al., 2010; Morales et al., 2013), NPs-TiO_2 and NPs-SiO_2 stimulated seed germination of *Triticum aestivum* and *Lycopersicum esculentum* (Feizi et al., 2012; Siddiqui & Al-Whaibi, 2014), NPs-ZnO stimulated plant growth and development of *Arachis hypogaea* (Prasad et al., 2012), increased the content of chlorophyll and geraral protein in *Cyamopsis tetragonoloba* (Raliya & Tarafdar, 2013).

Nanoinsecticides. Nanomaterials are promising for managing and controlling of pests in contemporary agriculture. The help of ethylene glycol with nanoparticle covering increased insecticide activity of garlic essential oil against *Tribolium castaneum* by 80% (Yang et al., 2009). Researchers have determined the high effectiveness of silver, aluminium, zinc and titanium nanoparticles against pests (*Tribolium castaneum*) and pathogens (Goswami et al., 2010). Toxicity of silicon nanoparticles against the rice weevil has been studied. It has been determined that the death rate of the pests reached 90%, which affirms their high efficiency. With efficiency of preparations, problems of environmental protection should be taken into account (Debnath et al., 2011). Most contemporary synthetic pesticides are highly toxic and have destructive consequences for the environment. Transition to nanoinsecticides will decrease incoming of toxic substances into the environment and it is very promising from the point of view of protecting the environment from pollution (Singh Duhan et al., 2017).

Nanofungicides. In the fight against plant phytopathogens, nanofungicides are used more and more often. Using silicon nanoparticles was more effective against microorganisms (*Aspergillus niger* and *Fusarium oxysporum*) on corn plants compared with traditional synthetic fungicides. Research on effectiveness of ZnO (40 nm), AgO (50 nm) and TiO_2 (95 nm) nanoparticles against *Macrophomina phaseolina* in oil crops have shown the high effect of Ag, Zn and Ti nanoparticles (Suriyaprabha et al., 2014). Ag nanoparticles have been shown to be most effective (Shyl et al., 2014). High antifungal activity of Ag nanoparticles compared with other nanometals was confirmed by researches of other scientists. Such effects are due to capability of Ag nanoparticles to penetrate into the cell of pathogenic fungi, disturb energetic exchange, breathing functions, provoke mutations of DNA, destroy ferments, provoke other negative processes (Kim et al., 2009; Velmurugan et al., 2009).

Nanoherbicides. A promising tendency in nanotechnologies is nanoherbicides development for purpose-oriented delivery of herbicides to the root system of weeds. Particles of nanoherbicides reached the root system of weeds, penetrated into cells, hindered the processes of metabolism. Eventually this led to plant death (Nair et al., 2010; Ali et al., 2014). At the same time, nanoherbicides which decrease pollution of the environment have been created. There has been research on toxicity of nanocapsules poly(ε-caprolactone) herbicides (ametryn, atrazine, simazine) compared to herbicides without capsules. Cytogenetic tests showed that toxicity of herbicide nanocapsules was lower compared to water plants *Pseudokirchneriella subcapitata* but increased a little as to *Daphnia similis*. On the whole, toxicity of herbicide nanocapsules was lower compared to herbicides without capsules (Clemente et al., 2014).

Ecotoxicity of nanomaterials and nanoparticles

At the same time alongside the positive peculiarities of nanomaterials, a large amount of research affirms their danger for the environment.

Physical and chemical properties of nanoparticles when they introduce into the environment change. These changes depend on pH surrounding, temperature, organic matter, clay in the soil and others. Their charge changes, adhesion to colloids, mineral and organic substances in water and soil appears. As a rule, organic matter neutralizes surface charge of nanoparticles. Humic asids prevent adhesion and decrease their toxicity. However, under the influence of abiotic factors and participation of living organisms the most complicated changes of nanomaterials take place, such as change of the ecological role of nanoparticles, reaction of biological systems to their influence and, as a consequence, their toxicity (He et al., 2015). Nanomaterials which reach the surface of the earth can pollute the soil and migrate into surface and groundwaters as well. Nanoparticles can be transferred into water systems by wind or come with rainfall (Ray et al., 2009). There are no data about potential consequences of influence of nanomaterials on natural ecosystems. The portion of nanomaterials in the soil is partly controlled by the processes of sorption by organic substances and destruction under the influence of solar radiation. Processes of nanomaterial destruction in the environment are still not examined (Turco et al., 2011).

According to the resolution of Organization for Economic Co-operation and Development (OECD), all chemical substances coming into environment as a result of human activity have to be subjected to ecotoxicological assessment (OECD Guidelines for the Testing of Chemicals, Section 3, Environmental fate and behaviour) (OECD Test Guidelines for the Chemicals, 2018).

For making decisions as to implementing nanotechnologies into agricultural practice we have to assess correctly the direction of changes of nanomaterial properties in the environment and make an objective prognosis of ecotoxical risks as a result of their use.

Toxicity of nanomaterials and nanoparticles for plants. It is reasonable to consider the influence of nanomaterials on plants at physiological and molecular levels (Marmiroli & White, 2016).

One of the ways nanoparticles enter the organism of plants is nanofertilizers, which contain nanoparticles in their composition. Nanoparticles from nanofertilizers get into plants and result in change of metabolism process of plants, cause stress, damage at cell level and to certain organs. Nanofertilizers Avatar-1 and Nano-gro in concentration of 0.025–0.200% have been studied. These nanofertilizers contained NPs Mg, Mn, Zn, Ag, Cu. It has been determined that for prognosis of' danger of nanoparticles it is necessary to study dependence "dose – effect" on the level of cell and its organelles. Research results showed that the nanofertilizers caused cytotoxic effect, which became evident in changing mitotic activity, duration of certain phases of mitotic cycle and influenced the size of meristematic tissue cells. At the early stages of plant development, nanoparticles stimulated the processes of growth. However, in the process of growth and development of plants their inhibitory action became evident, which became stronger with increasing of preparation dose and reached 56% relative to control. It has been noted that toxic action of nanofertilizers depends on size and shape of the nanoparticles which they contain. Nanoparticles of smaller size were more toxic, crystal nanoparticles were more toxic compared to amorphous nanoparticles (Makarenko et al., 2016).

Genotoxic and phytotoxic effects NPs of cerium ($nCeO_2$) and titanium ($nTiO_2$) were researched on sprouts of barley (*Hordeum vulgare* L.). Concentration from 0 to 2000 mg/L was studied during seven days. Genotoxicity was researched according to index of DNA polymorphism (RAPDs), mitotic index was studied according to changes of cells on root tips. Negative influence of nanoparticles on RAPDs as well as on the level of chromosomes (decreasing of cell division) has been noted. $nCeO_2$ induced changes in chromatin and nuclei of plant roots. On cell level, ATP (adenosine triphosphate) changes have been noted. Toxicity of $nCeO_2$ was higher than $nTiO_2$. General microanalysis allowed ascertainment of the presence of $nCeO_2$ and $nTiO_2$ root cells of barley (Mattiello et al., 2015).

Nanoparticles of zinc oxide influence *Pisum sativum* L. Authors observed the influence of NPs ZnO on photosynthesis, colouring agents, proteins, carbohydrates. It has been determined that nanoparticles can cause general phytotoxicity (Arnab et al., 2016).

Phytotoxicity of NPs ZnO and TiO_2 as to the rice root system (*Oryza satyva* L.) was controlled according to parameters: seed germination and root length. It has been determined that nanoparticles did not influence seed germination. However, zinc oxide had a negative influence on the development of the root system (Boonyanitipong et al., 2011).

Generally, phytotoxicity becomes apparent as a result of entry of NPs through the plant root. A question arises: can NPs come into plants from the atmospheric air through the leaves? Information about such processes is limited as there are not enough experimental results, which is an obstacle for detection of the risks of phytotoxicity from NPs. For determining the ability of absorption of NPs through leaves, research on cucumbers (*Cucumis svenvus*) was conducted. The leaves were treated with powder of nano cerium ($nCeO_2$) in concentration of 0.98 and 2.94 g/m^3 and suspension in concentration of 20 to 320 mg/L. In 15 days after treatment, absorption of $nCeO_2$ and activity of ferments which cause stress were analyzed. Presence of $nCeO_2$ was detected in all plant organs as well as in the root. The research results affirm the possibility of entry of nanoparticles through leaf surface of plants and appearance of phytotoxic effect (Hong et al., 2014).

Introduction of a mixture of nanometals (ENMs) into the soil and their influence on the growth of *Medicago truncatula* and on soil microorganisms, in symbiosis with *Sinorhizobium meliloti*, has been investigated. It was determined that ENMs that came from the soil into plants accumulated in different organs and influenced the processes of growth and development. Considerable changes in the structure of microbial cenosis of the soil were also determined (Judi et al., 2015).

Comparative cytotoxicity of metals and nanoparticles (As, Cd, Cr, Hg, Fe i metal-NP) through autophagy of cellshas also been analysed. Nanoparticles were observed as a powerful inducer of autophagy in a few cell lines. The inhibition in the context cell response to nanoparticles was determined (Chatterjee et al., 2014).

Research on toxicity of nanometalshelped determining certain peculiarities of their influence on plants: NPs-TiO_2 were obstacles to cell growth and depressed the processes of nitrogen fixation (test-plants *Anabaena variabilis*) (Cherchi & Gu, 2010), reduced the energy of germination (test-plants *Triticum aestivum*) (Feizi et al., 2012); NPs-Al were obstacles to root growth (test-plants *Lolium perenne*, *Zea mays* and *Lactuca sativa*), reduced the energy of germination (test-plants *Lolium perenne*) (Lin & Xing, 2007); NPs-Ag disturbed the processes of mitosis, changed passing metaphases, changed chromosomes, destroyed cell walls (test-plants *Allium cepa*) (Kumari et al., 2009), changed the processes of transpiration (test-plants *Cucurbita pepo*) (Stampoulis et al., 2009), depressed growth (test-plants *Linum usitatissimum*, *Triticum aestivum*) (El-Temsah & Joner, 2012; Dimkpa et al., 2013); NPs-Zn were obstacles to root growth and development (test-plants *Zea mays*, *Cucumis sativus*, *Lactuca sativa*, *Raphanus sativus*, *Brassica napus*, *Lolium perenne*) (Lin & Xing, 2007), reduced the energy of germination (test-plants *Zea mays*) (Lin & Xing, 2007); NPs-Cu were obstacles to seed germination (test-plants *Phaseolus radiatus*) (Lee et al., 2008), reduce biomass formation and were obstacles to root growth (test-plants *Cucurbita pepo*) (Stampoulis et al., 2009); NPs-Al_2O_3 were obstacles to root growth (test-plants *Zea mays*, *Cucumis sativus*, *Brassica oleracea*, *Daucus carota*) (Yang & Watts, 2005; Lin & Xing, 2007).

Toxicity of nanomaterials (nanoparticles) for soil organisms. The question of possible toxic influence of nanomaterials (nanoparticles) on soil organisms has arisen quite sharply. Nanoparticles can come into the soil from natural sources and as a result of human activity – from nanofertilizers, nanoherbicides, nanofungicides and nanoinsecticides.

For testing chemical substances and soil pollution resolutions the OECD in Europe and USEPA (Environmental Protection Agency) in the USA recommend first of all using the earthworm *Eisenia fetida* (OECD Test Guidelines for the Chemicals, 2018). In case of need we can use species which are characterized with high sensitivity such as *Lumbricus terrestris* and *Apporectodea caliginosa* (Fitzpatrick et al., 1996).

A necessary condition for determining the ecological risk of NPs is that laboratory experiments are designed to be as close as possible to natural conditions. In the conditions of laboratory experiments it has been determined that adding the salt of ZnO NPs to nutritious medium caused increasing bioaccumulation of ZnO for the worm *Eisenia fetida*. A high level of mortality was observed at concentration of ZnO 50 mg/L. We used a solution which was an analogue to soil extract instead of distilled water. Hereby, toxicity of ZnO NPs decreased greatly (Li et al., 2011).

Nanoparticles can be present in the environment for a long time and affect the organisms in the ecosystem negatively. To assess their danger it is important to know about consequences of prolonged usage. In the conditions of prolonged laboratory experiment the reaction of *Eisenia fetida* to the influence of CeO_2 NPs and cerium salts was researched. Influence of nanoparticles of cerium oxide in size of 5 to 80 nm and cerium salts in concentration ranging 40 to 10,000 mg/kg was studied. It was determined that CeO_2 NPs during the period foreseen by standard test do not influence *Eisenia fetida* negatively. However, the results of histological researches showed possibility of negative changes in future

(Lahive et al., 2014).

Concentration of NPs in the soil and their qualitative content play a significant role for soil organisms. NPs TiO_2 and ZnO are toxic for *Eisenia fetida*. It has been determined that concentration of TiO_2 and ZnO over the level of 1.0 g/kg in the soil is dangerous. This is affirmed by the activity of antioxidant ferments and indices of destruction of mitochondrions. It has also been determined that toxicity of ZnO NPs was higher for earthworms than TiO_2 NPs (Hu et al., 2010).

Eisenia fetida has been used to check toxicity of some non-organic (Ag, Cu, Ni, Al_2O_3, SiO_2, TiO_2 i ZrO_2) nanoparticles (NPs) and their metal salts and metal oxides. Concentration of 1,000 mg/kg was investigated. It has been established that toxic effects were caused only by Ag-NPs, Cu-NPs and TiO_2-NPs (Heckmann et al., 2011).

Reaction-response of *Eisenia andrei* showed analogous toxicity of Ag-NPs and Ag nitrate. However, they observe higher absorption of Ag from Ag-NPs in the earthworms was observed than Ag absorption from nitrates. Thus, it can be predicted that Ag-NPs toxicity would increase in a long-term experiment (Schlich et al., 2013). Toxicity of silver nanoparticles depended on their size and shape. Toxicity decreased with increasing the size of particles. Particles in the shape of truncated triangle had higher effect of toxicity than those of spherical and rod shape (Panáček et al., 2006; Pal et al., 2007).

Important test-objects for studying toxicity of NPs are soil microorganisms and soil ferments. They affirm the direction of the processes of mineralization and synthesis of the matters in the soil. Research was conducted on agricultural soils treated with nanoparticles SiO_2, ZnO, TiO_2 and CeO_2 in concentration of 1 mg/g. Toxicity was assessed according to quantity of functional groups of microorganisms and activity of soil ferments. NPs ZnO and CeO_2 caused decreasing of quantity of bacteria species *Azotobacter* and bacteria which take part in transformation of phosphorus and potassium. Depression of activity of soil ferments in soil was observed. At the same time, nanoparticles of SiO_2 stimulated positive microbiological processes in the soil (Chai et al., 2015).

Nanomaterials can bioaccumulate and be transferred along trophic chains. Some authors point out that risk assessment of nanomaterials must not be based only on short term experimental results. Efforts must also be made for conducting long-term experiments (McKee & Filser, 2016).

Nowadays there are no standard methods for studying toxicity of nanoparticles for soil organisms and processes taking place in the soil. Soil is an important component of the environment which influences its contiguous surroundings (air, underground and surface waters). Using modern methods, in particular Pearson's correlation, a close correlative connection between thermal and dynamic parameters and quantity of functional groups of bacteria and the activity fermentshas been determined. It has been shown that such interconnection can be successfully used for testing toxicity of nanoparticles in agricultural soils (Chai et al., 2015).

Toxicity of nanomaterials (nanoparticles) for insects. Extensive use of nanomaterials in agriculture has led to their considerable influence on all representatives of ecosystem, including insects. For guaranteeing ecological safety of modern preparations, it is necessary to understand mechanisms of influence of nanoparticles on insects and prevent their negative effects.

Prolonged consequences of using carbon nanomaterials on the insect *Spodoptera frugiperda* have been researched. Larvae of these insects were kept on a diet which contained nanomaterials in concentrations of 0–1000 μg/g. The results showed that concentration of CNMs in the diet of the larvae had negative influence on reproductive characteristics, digestion system and metabolic activity. The diet with the highest concentration of CNMs worsened considerably the parameters which characterized fecundity of insects (Carlos et al., 2018).

The influence of silver nanoparticles AgNPs on growth and development representatives of different insect species such as *Spodoptera litura* and *Achaea janata* has been determined. For this purpose, leaves of the plant *Ricinus communis*, which were the source of nutrition for insects, were treated with nanoparticles AgNPs and salt $AgNO_3$. It was established that a small amount of nanosilver accumulated in the intestinal tract of larvae and pupae but most of the nanoparticles were removed from the organism. Research using electronic microscopy showed that nanoparticles of silver accumulated in organelles. Differences in activity of antioxidant ferments of the intestine were found, which indicates the presence of oxidizing stress in the insect organism (Jyothsna Yasur et al., 2015).

Nanoparticles of silver can have a negative effect on viability and considerably decrease the weight of the caterpillar *Helicoverpa armigera*. It has been established that nanoparticles of silver have a high effect on protease ferments. At concentration of 100 μg AgNPs, activity of protease ferments decreased by 50–70% (Saware Kantrao et al., 2017).

Toxicity of silver nanoparticles Ag NPs for insects was confirmed in experiments with larvae, pupae and adults of the fly *Drosophila melanogaster*. Concentrations of 10–200 ppm were studied. It has been determined that AgNPs had a negative influence on the processes of vital activity of *D. melanogaster*, depressed the development of larvae and increased the level of mortality (Salah-Eddin et al., 2015).

Along with AgNPs, ZnONPs were characterized with toxic influence on insects as well. Nanoparticles with size of 10–30 nm were studied. It was determined that ZnONPs caused decrease of proteins, carbohydrates and lipids in larvae of *Spodoptera littoralis*. They induced activity of amylase, lipase, catalase and other antioxidant ferments. ZnONPs influenced the development of *S. littoralis* by changing the physiological processes of digestion and disturbance of immunological characterstics (Ahmed & Ali, 2018).

Toxicity of nanomaterials (nanoparticles) for water organisms. As a result of a migration, nanomaterials (nanoparticles) can enter surface and groundwaters and affect water organisms. Many scientists are now investigating these processes and phenomena.

For water organisms, toxicity of nanometals can be higher than of salts of these metals. Nanometals are especially dangerous at the early life stages of water organisms. Researches have shown that mortality level of metal NPs for fish is in the range of mg-μg/L. It has been proved in a 48 hour experiment that LC_{50} of NPs Cu for juvenile zebrafish was – 0.71 mg/L, and for soluble salts of Cu^{-1} – 0.78 mg/L. It is assumed that the higher level of toxicity for NPs Cu is conditioned by peculiarities of their physical and chemical constitution and peculiarities of mechanisms of influence on living organisms. Similar results have been received for Ag-NPs, Cu-NPs and ZnO-NPs: nano forms of metals were more toxic for embryos and small fry of fish than equivalent salts of metals. The authors concluded that nano forms of metals have greater toxic influence on physiological processes of water organisms than traditional metal solutions (Shaw & Handy, 2011).

There is a connection between bioaccumulation of nanometals and their toxicity. Accumulation of CuO and CuO NPs in the freshwater snail *Lymnaea stagnalis* has been studied. It has been established that 80–90% of CuO NPs bioaccumulated in the organism of *L. stagnalis*. Soluble copper oxide (CuO) had considerably lower ability to bioaccumulation. According to reaction of *L. stagnalis* it has been shown that CuO NPs were considerably toxic compared to CuO (Croteau et al., 2014).

For prognosis of ecotoxicity of nanoparticles, the question of their distribution in the organism is very important. According to results of researching the influence of NPs on water organisms it has been determined which organs accumulate them the most. It has been established that after ingestion nanoparticles enter the blood-vascular system. From the blood-vascular system they penetrate other organs. Most of them accumulate in the intestine, liver and reproductive organs (Lavelle at al., 2015).

For researching ecotoxicity of nanoparticles it is recommended to use as a test-organism the embryo of zebrafish (*Danio rerio*). The response of *Danio rerio* to AgNPs and $AgNO_3$ has been studied. Correlation was found between accumulation of nano silver and lethal outcome (Böhme et al., 2015). Analogous results were obtained by researches on AgNPs and $AgNO_3$ for seaweed *Euglena grarilis* (Li et al., 2015).

Using test-organisms, toxic concentrations for 12 nanomaterials: Al_2O_3, Co_3O_4, CuO, Fe_3O_4, MgO, Mn_3O_4, Co_2O_3, SiO_2, ZnO, TiO_2, WO_3 and Pd has been determined. For testing, we used such microorganisms as *Vibrio fischeri*, *Escherichia coli*, *Staphylococcus aureus*; seaweeds *Pseudokirchneriella subcapitata* and protozoa *Tetrahymena thermophila*. Toxic influence of nanoparticles for 10 substances was observed under concentration 0.1–58 mg/L. Nano MgO, Al_2O_3, SiO_2, WO_3 and Sb_2O_3 in concentration of 100 mg/L were not toxic for most of water organisms (Aruoja et al., 2015). Toxic influence of nanoparticles of gold on water organisms *Shewanella oneidensis* and *Daphnia magna* has been established (Qiu et al., 2015).

For determining ecological risk from chemical substances in aquatic environments it is necessary to conduct prognosis of their concentration, which is difficult to do for nanomaterials. Assessment of nanomaterial exposure depends on nano-specific processes. Subsidence and dissolution are important for removing nanomaterials. First order removal kinetics are adequate for modeling nano-removal processes (Quik et al., 2011).

Thus, results of numerous researches affirm the toxic influence of nanomaterials and nanoparticles on water organisms, which makes ecotoxicological research on nanoagrochemicals and nanopesticides obligatory.

Nanoecotoxicology: problems and assignments

Nowadays, there is no system for determining ecotoxicity of nanoparticles. There is an urgent necessity to develop corresponding programmes. To solve this problem, it is reasonable to follow the main recommendations. Firstly, research must improve our knowledge of ecotoxicity of ENMs by choosing test objects and concentrations correspondent to reality. Secondly, testing must take place at different stages of biosystem organization with feedback. Thirdly, a large number of specialists such as analysts, modelers, ecotoxicologists, government, producers, and academic researchers must be induced to cooperate in conducting ecological assessment of the danger of nanotechnologies (Holden et al., 2016).

Currently, general biological approaches are used for development of nanoecotoxicology. Prognostic models of nanomaterials behaviour in biological systems must be taken into account. For this purpose, traditional approaches for assessment of changes in genes, proteins and metabolite creation can be used (Rösslein et al., 2015). Research has to be directed to the realization of a system of nanotoxicology as well as mechanisms of nanomaterial risks assessment (Costa & Fadeel, 2016). Using analysis of cause and effect (C&E) of cytotoxicity is promising for nanomaterials testing.

Scientists are examining the approaches to studying the toxicity of nanomaterials. They distinguish quantitative and qualitative approaches. Quantitative approaches involve development of methodologies at the molecular level under using spectral and colorimetric methods, spectroscopy and plasma mas-spectrometry. It is proposed that a new integration approach should be adopted using methodology of mapping synchronic emission of radiographic fluorescence analysis. Also promising are the methods of hyper-spectral microscopy, which show a great potential for assessment of spatial division and spectral characteristics of nanoparticles in biological and ecological systems, which favours investigating their role and transformation in different surroundings. Qualitative approaches are examined as valuable supplements to quantitative researches (He et al., 2015).

For measuring the concentration of nanoparticles in water, it is proposed to use precise spectrometry, which will allow quantitative determination of nanoparticles (especially nC_{60}) and their transformation to be conducted. This method allowed concentration of nanoparticles and transformation products to be determined at the level of 5 ng/L (Wezel et al., 2011). There is a proposal to monitor nanoparticles in water using the method of electronic microscopy. Applying this method allowed the authors to determine concentration of nanoparticles of dioxide titanium in the water of the Danube Lake (Vienna, Austria) (Gondikas et al., 2014).

Infra-red spectroscopy and fluorescent microscopy are highly sensitive to specific fluorescent colouring agents and under some stimulation, it is one of the most effective ways of identification of different nanomaterials *in vivo/in vitro* (Mudunkotuwa et al., 2014). At present, the main directions of experimental research are studying of translocation/division of nanomaterials in biotic/non-biotic systems, studying migration to biota and humans, revealing and monitoring quantity of entry of nanomaterials into the environment, studying interaction between physical and chemical properties of nanomaterials and nanotoxicity. Methods of modeling are used more and more often (He et al., 2015).

Mathematical models are necessary for assessment of the concentration of nanoparticles (NPs), which come into environment as a result of human activity. Dale et al. (2015) presented an ecological model for the James River Basin, Virginia, which describes changes in concentration of zinc oxide (ZnO) and silver (Ag) NPs. The authors emphasize that "the first generation" of risk model of NPs probably describes their influence in freshwater rivers inaccurately because of the low separating power of the model and simplification of changes in chemistry.

Modelling of behaviour of nanoparticles in the natural environment allowed criteria to be established which can be used for predicting consequences of influence of nanoparticles of Ag, TiO_2, SiO_2, ZnO, Al_2O_3, montmorillonite, Al_2 on the environment. They are hazardous effects, stability during incineration, tendency for sedimentation, dissolution in water (Som et al., 2011).

Using nanomaterials demands conscious efforts for establishing, keeping resolutions in production, and utilization of these synthetic chemical substances. Preventive measures must be taken by researchers and scientists as well as controlling organs in order to minimize potential dangers and maximize advantages for people (Chai et al., 2015; He et al., 2015). Safe controllability and utilization of nanomaterials is receiving more and more attention from both state and governmental authorities. The Organization for Economic Co-operation and Development (OECD), the United States, England, Germany, the European Commission and Australia have developed regulations as to safe treatment of nanomaterials. However, there are still a lot of organizations which use the usual chemical methods of security for nanomaterials (He et al., 2015).

The OECD Guidelines for the Testing of Chemicals presented about 150 of the most actual internationally coordinated methods of testing chemical substances which are used by state, industrial and independent laboratories for determining and marking potential hazards. They are the set of instruments for professionals which are used first of all in regulatory tests of security for subsequent registration. This group of tests contains questions on the ecological role and behaviour of chemical substances. In 2017 chapter 3 "Degradation and Accumulating" was changed into "Environmental Fate and Behaviour" to take into consideration leading directions, measuring final points such as dispersion and aggregation (OECD Test Guidelines for the Chemicals, 2018).

A very important direction of research – nanoecotoxicology was formed in the last decade. It is connected with the rapid development of nanotechnologies, introduction of nanoparticles into the environment and uncertainty about their influences on natural ecosystems. The authors accentuate that nanoecotoxicology has to investigate sources of entry of nanoparticles into the environment, their transformation, bioaccumulation, influence on living organisms from cell to community leval. This information must be used for determining ecological risks from nanotechnologies.

Nowadays nanoecotoxicology faces a large number of problems. It has to solve the problem of bioaccessibility, peculiarities of distribution of nanoparticles in the organism, to determine sensitive targets and to investigate interaction with bioreceptors. Taking into account the vast diversity of nanomaterials, their type, size and shape, it is impossible to check toxicity of each nanomaterial. Nanoecotoxicology has to develop a multilevel strategy of testing which will allow transfer of knowledge received about one organism in precisely determined conditions to more complex scenarios of ecological systems (Schirmer & Auffan, 2015).

Conclusion

Analysis of literature allows us to say for certain that nanotechnologies have found their use in all fields of human activity including the agrarian sector. Their importance is increasing taking into account climate changes, the need to provide humanity with food and environmental pollution. High effectiveness of nanotechnologies in the sphere of creating preparations for crop cultivation has been proved. Nanofertilizers, nanofungicides, nanoinsecticides and nanoherbicides have a number of economical and ecological advantages. At the same time, nanopreparations contain nanoparticles which can have negative influence on plants and other organisms in natural ecosystems.

It has been established that in higher plants nanoparticles provoke such negative effects as inhibition of cell growth and nitrogen fixation activity, decreased mitosis, disturbed metaphase, sticky chromosome, cell wall disintegration and breaks, reduced transpiration, reduced seedling growth, reduced biomass and root growth and others.

For soil and water organisms, nanoparticles are characterized by a high level of bioaccessibility, bioaccumulation and toxicity. Their entry into an organism is accompanied with disturbances in physiological processes, destruction of mitochondria and DNA and emergence of lethal effects. Toxicity depends on qualitative and quantitative content of nanoparticles, their concentration, size and shape.

In the last decade, a very important direction of research – nanoecotoxicology was formed. However, to solve the problems of nanoecotoxicology general biological methods are mainly used. Nanoecotoxicology has to solve the problem of bioaccessibility, peculiarities of distribution of nanoparticles in the organism, to determine sensitive targets and, to investigate interaction with bioreceptors and develop a multilevel strategy of testing. Preventive measures must be taken by researchers and scientists as well as by controlling authorities in order to minimize potential hazards and maximize the advantages of nanotechnologies for humanity.

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